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Synthesis and Characterization of Aluminum Alloys with Metal Oxides (CuO_2) Additions as Reinforcement

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Abstract

In this investigation, the addition of several amounts of metal oxide particles (CuO_2) in Al matrix is carried out due to the need to improve the mechanical properties such as the ductility of aluminum for applications in the electrical sector. Samples were obtained by means of a stirring casting process. From the results of the microstructural characterization, it was observed that the metallic oxides induce the modification of the dendritic structure and grain refinement. X-ray diffraction characterization mainly shows the formation of Al_2CuO_4, Al_2O_3 and CuO compounds. Mechanical properties showed that the different thermal treatments resulted in an improved hardness, from 30 kg/mm^2 for the un-reinforced sample to 90 kg/mm^2 for reinforced samples. The addition of metallic oxides in the Al matrix produces an improved electrical conductivity specifically in sample with 0.50 g of CuO_2 additions.

Keywords

Electrical Properties, Oxides Additions, Soft Alloys, Mechanical Properties

1. Introduction

In particle-reinforced materials, two groups of materials are included: The first is based on transition metal matrices and the second on soft or light alloys [1] [2]. The purpose for which the composite materials were developed is to obtain enhanced properties such as: density, good tensile strength, high modulus of elasticity, low coefficient of thermal expansion, complicated to achieve with a monolithic material [1]-[6]. The final result will depend on the properties of the matrix and the reinforcement, on the properties of the lightweight materials. An excellent combination can result through the combination of low melting point, good mechanical properties and low density (2.7 g/cm^3) as aluminum-based alloys, these characteristics are currently needed mainly in structural applications such as aeronautics, military and transport. The addition of hard particles in a soft metallic matrix, results in a compound with combined properties, this will improve the mechanical properties of the compounds, for their different applications [2] [7]. In the last decades the reinforcement of the aluminum matrix has been studied [8] [9] [10], adding reinforcements ranging [10] [11] [12] [13] from Nb_2O_5, CuO, ZnO, SnO, Cr_2O_3, TiO_2 or MgO [14] [15] [16] [17] to unconventional reinforcements, such as quasicrystals [18] [19]. All these reports show the improvement of mechanical properties. The novelty of this work is to generate information related to the addition of reinforcing oxides particles, namely CuO_2 into the aluminum matrix, analyzing their effect on the microstructure, mechanical and electrical properties of the resultant alloys, due to the very little information existent related to this system, due to limited information existent in the literature about this alloy and therefore the need to improve the mechanical properties such as the ductility of aluminum for applications in the electrical sector.

2. Experimental Procedure

Aluminum (99.99) was used as matrix material and different concentrations of CuO_2 particles (0.15, 0.25 and 0.50 g) were added as reinforcing components into the liquid alloy followed by stirring with a stainless steel flat bar at 250 rpm. The resultant alloy was cast into a copper mold with a rectangular shape. To study the microstructure, 1 × 1 × 1 cm samples were cut, grinding with sand paper up to 600 grade and polishing with alumina paste 0.3 μm and then using the Dix-Keller etching reagent to reveal its microstructure. Surfaces images were obtained using an Olympus optical microscope in dark field mode. XRD analyzes were performed in a BRUKER diffractometer to obtain identification of the phases present. The hardness Vickers tests were carried out using a Leco 300 MT equipment, average hardness values were obtained using a load of 0.1 kgf with a time of 15 s according to ASTM: E384 standard. Different heat treatments were carried out in the AR-340 FELIZA furnace, as shown in **Table 1**. For the study of electrical properties a RIGOL 3058E Micro-ohmmeter was employed.

3. Results and Discussion

3.1. Microstructural Characterization

It is observed in **Figure 1**, the microstructures for samples with Aluminum plus different CuO_2 additions, where in **Figure 1(a)** it is observed a dendritic behavior with 0.15 g additions of CuO_2, being the dendrite size of approximately 45 μm. For the case of sample with 0.25 g of additions of CuO_2 in **Figure 1(b)** it can be observed a dendritic behavior, where dendrites present an enlargement in its structure being the dendrite size of 90 μm average. On the other hand for sample with 0.50 g it can be observed its microstructure in **Figure 1(c)** that exist an evolution of the dendritic structure to equiaxed grains. Hence, the effect of the oxide additions it is clearly observed for the three different compositions where copper oxides promote de grain growth [1]. Microstructural variations are explained considering that oxides additions may induce the modification of the dendritic structure and grain growing under the mechanism that particles during the solidification process acts as nucleation points on which the aluminum grains solidify [2] [3] [4].

3.2. X-Ray Diffraction Analyses

The X-Ray Diffraction patterns are presented in **Figure 2**, in it can be observed different peaks corresponding to the compounds formed during the melting process.

The proposed chemical reactions developed during the melting-casting-solidification process are as follow:

$$4Al + 3CuO_2 \rightarrow 3Cu + 2Al_2O_3 \quad (1)$$

$$Al + 2CuO_2 \rightarrow 2CuO + AlO_2 \quad (2)$$

$$2Al + 2CuO_2 \rightarrow Cu + Al_2CuO_4 \quad (3)$$

Table 1. Alloys designation and description of heat treatments.

Nomenclature	Description	Parameters
AM	Aluminum Matrix	
BA	As-cast alloys	Addition 0.15 0.25 0.50 g
AA	Annealed in Air	300˚ - 600˚C 12 h
AAA	Annealed in an argon atmosphere	600˚C 12 h
OQ	Oil quenched alloys	500˚C 1 h
BQ	Brine quenched alloys	500˚C 1 h
OQT	Oil-quenched + tempered	260˚C 1h
BQT	Brine-quenched + tempered	260˚C 1h

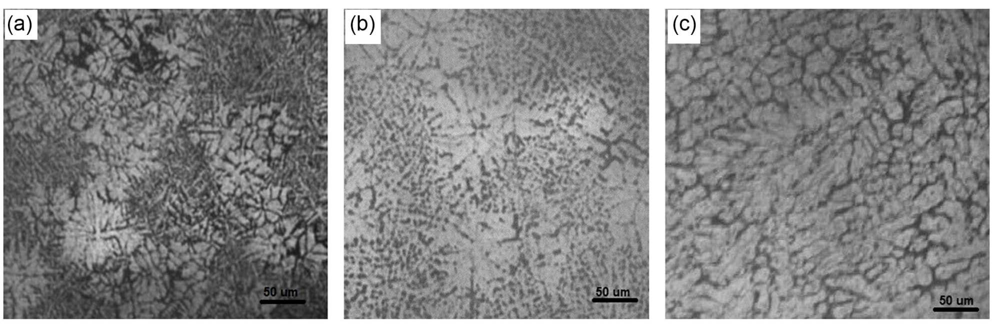

Figure 1. Optical micrographs of the alloys structures with different compositions. (a) 0.15 g. (b) 0.25 g and (c) 0.50 g.

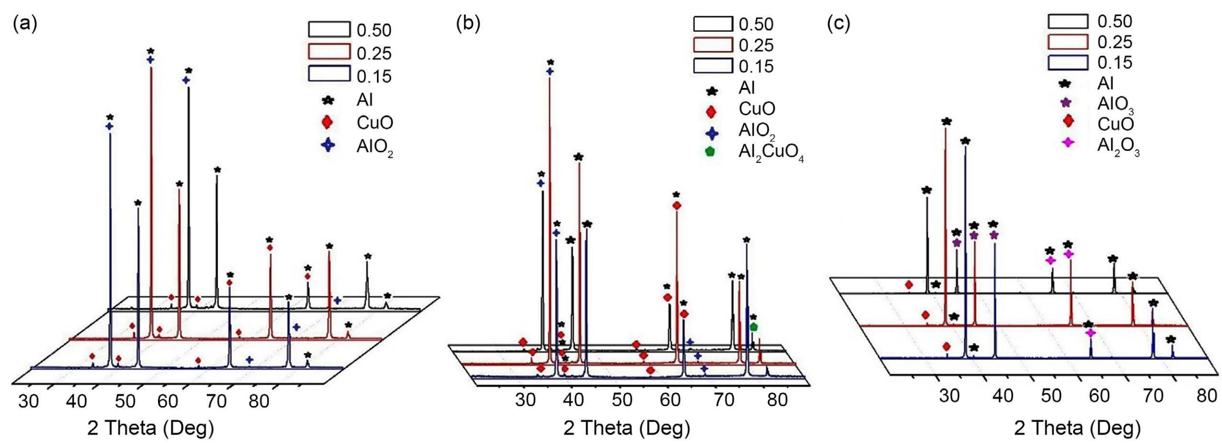

Figure 2. X-ray diffraction pattern of BA, AA and AAA samples with their respective additions.

It can be observed in the three possible reactions that Al and copper oxide produces the aluminum oxide plus copper, due to the dissociation of the oxygen present in the CuO_2. The proposed reaction mechanism of formation is the interfacial reaction of the oxygen of the CuO_2 with the liquid aluminum [6]. It is noticeable that the aluminum oxide (Al_2CuO_4) in Equation (3) is product of an overheating in the system and the agitation produced by the stirring process that permit a constant external detachment of the superficial layer of the CuO_2 particles.

In **Figure 2(a)** it is observed the diffraction peaks for samples with different CuO_2 particles additions without heat treatment, where is observed that that during the melting process are generated mainly two types of oxides; CuO and AlO_2. On the other hand, when alloys with different CuO_2 particles are exposed to annealing treatment (see **Figure 2(b)**), predominantly Al_2CuO_4 is generated. Finally, as can be seen in **Figure 2(c)** the change of atmosphere of heat treatments allows the creation of new metal oxides in very small quantities such as AlO_3 and Al_2O_3, this effect is attributed to an absence of oxygen in the furnace chamber [3].

The particles size obtained from the X-ray diffraction spectrum was determined by measuring the average percentage of the width at half height (FWHM) of the characteristic peaks, for each of the alloys reinforced with different CuO_2 additions and with different heat treatments. **Figure 3** shows the percentage of the width of the peaks corresponding to each of the alloys; for as-cast alloys (BA) it was observed that the higher the amount of oxide additions, the higher the amounts of resultant aluminum and copper oxides.

After annealing for 12 h, the oxides maintain the same behavior and in the sample AA 0.50 a lower amount of AlO_2 is generated, but a peak corresponding to copper and Al_2CuO_4 is shown with a width of 2.10% which is attributed to be affected by the amount of CuO_2 existing in the alloy [7]. Annealing in an argon atmosphere reduces the creation of different oxides in all alloys; Compared to BA, CuO_2 decreased for the alloy AAA 0.15 by 40.33%, AAA 0.25 by 58.94% and AAA 0.50 by 54.28% and for AlO_2 90.08%, 75.32% and 79.41% respectively. The

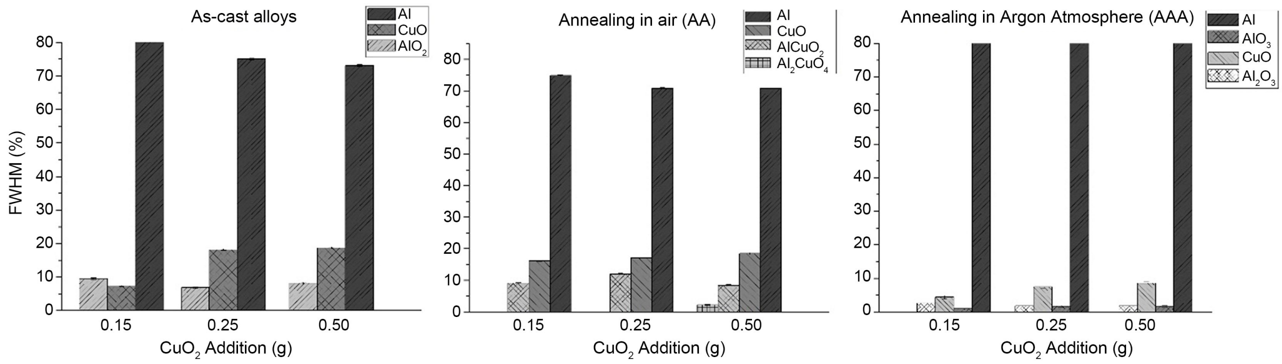

Figure 3. Percentage of peak width for alloys with different heat treatment, showing the percentage of detected compounds.

previous data, allowed us to obtain as a result the average crystallite sizes calculated for each alloy, supposing that the fluctuation in hardness is inversely proportional to the average crystal size.

3.3. Mechanical Characterization

3.3.1. Vickers Hardness

For soft matrix composite materials particles reinforced, the selection of the region in the sample where the hardness is evaluated is critical as the reinforcement phase should be considered. In **Figure 4** it is observed the plot of the hardness results AM equal to 30 kg/mm^2 while BM25 alloy possesses a hardness value close to 80 kg/mm^2.

The Bouvard [20] postulation stablish that small amounts of fine reinforcing particles cover the surface of coarse metal powders; this may be the reason for the increased hardness sample; as well as the combined effects of the distribution of oxide particles that act as obstacles in the dislocations movement, in addition the localized deformation of the materials take into account the presence of intrinsic porosity in the materials [20]. Therefore, the elevated hardness it is attributed to a reduced grain size [14], as shown in the plot. However, in samples BA50 the hardness slightly decreases, this is attributed to the dispersion of particles, creating a solid solution with uniform granular structure and average grain size of 25 μm, allowing an increment in plastic deformation.

3.3.2. Vickers Hardness Variation in Annealing Condition

Figure 5 shows the plot of the hardness of samples at the three different compositions of CuO_2 additions against of annealing at four different temperatures, in it can be observed that the higher the temperature, the greater the plastic deformation for all the alloys, in other words a decrement in hardness is observed, reaching a state of equilibrium from 500˚C. Samples AA 0.15 and AA 0.25 obtain their maximum hardness at 300˚C above the initial hardness of the AM, unlike the sample AA 0.50 where the hardness value is lower at this temperature.

For annealing in an argon atmosphere, a rectangular of steel chamber was manufactured and designed, which was adapted to the furnace where the Argon was recirculated during the 12 h of annealing at 600˚C. In **Figure 6** is presented

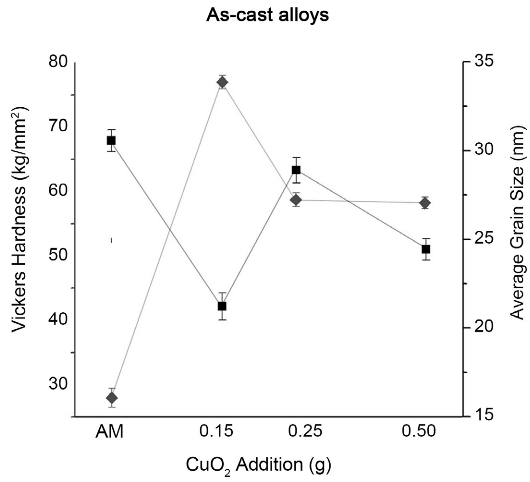

Figure 4. Hardness of alloys with different CuO_2 Additions as a function of the grain size.

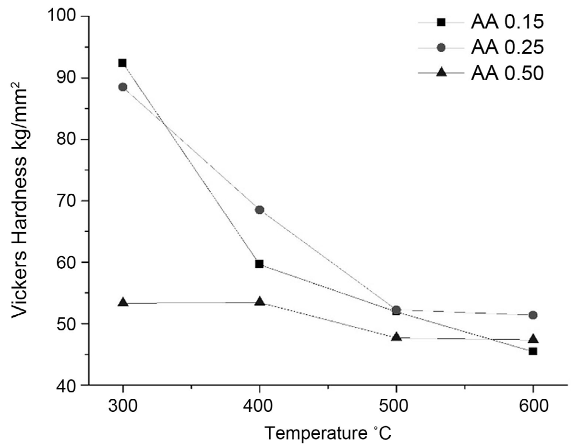

Figure 5. Hardness of the annealed samples with different concentrations of CuO_2 additions at different temperatures.

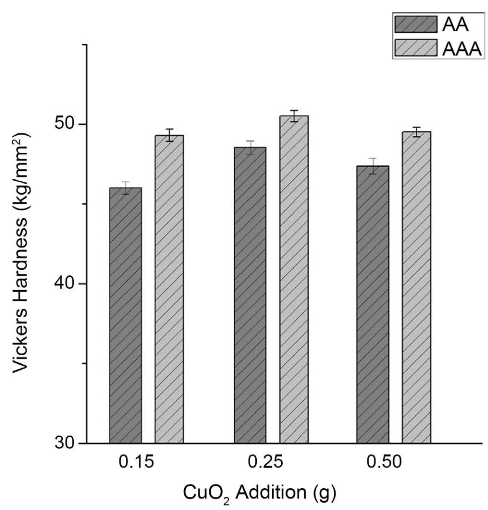

Figure 6. Hardness variation of annealed samples at 600˚C as a function of the atmosphere.

the hardness variations of the AA samples under annealing with different atmosphere at a temperature of 600˚C. Annealed alloys maintain the same behavior as samples annealed in an argon atmosphere, but their hardness is lower, this is attributed to the amount of the new oxides generated during heat treatment.

3.4. Electrical Characterization

It is well known that electrical resistance of a material is proportional to the electrical resistivity and is inversely proportional to the electrical conductivity [21]. In plot of **Figure 7** it can be observed a horizontal line that denotes value of the electrical conductivity of aluminum, this resulted 3.5 S/m at 20˚C, taking this value as a reference, it can be observed that copper dioxide addition in combination with the different heat treatments tends to increase the electrical conductivity. As it is well known, copper oxides are included in the family of superconductors [22] [23] and are called high temperature superconductors since they exhibit superconductivity at approximately 195˚C. For the OQ samples with 0.15g CuO_2 addition oil tempered it is observed that it keep the electrical conductivity close to the value of unalloyed aluminum. The decrease in electrical conductivity for the rest of the samples with this addition has been attributed as a result of the gradual increase in the number and size of particles of CuO_2, which leads to a decrease in the conductivity of the composite material due to the electrons dispersion; this effect has been correlated with impurities in aluminum matrix [21] [22].

For the samples with the addition of 0.25 and 0.50, it is observed that the AA, AAA and OQT samples the conductivity increases, this is attributed to the low index of precipitates in the surface area that which produces a partially freeway effect on the matrix [22], for consequence this phenomena generates an increment in electrical conductivity values.

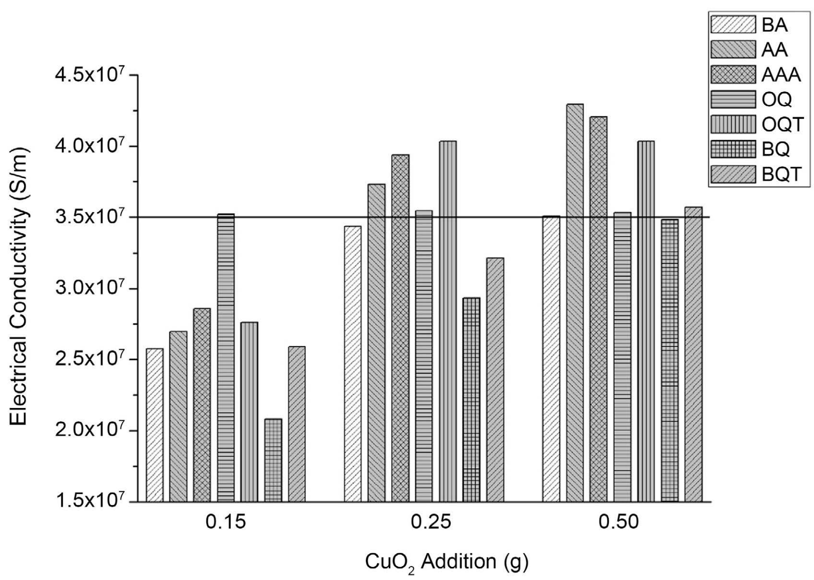

Figure 7. Plot of the electrical conductivity variation for samples with different heat treatments and different CuO_2 additions.

On the other hand, the non-linear correlation of the electrical conductivity with the hardness perhaps is the result of the differences in response of the hardness with the thermal treatments, which has been affected via generation of copper and aluminum precipitates with different size and randomly dispersed, created during the different aging stages [22] [23].

4. Conclusion

Aluminum alloys with CuO_2 particulates were obtained successfully by melt stirring process. A dendritic structure from fine to coarse was obtained depending of the amount of copper oxides added. Particularly, addition of 15 g of CuO_2 increases the hardness of the aluminum accompanied with a heat treatment of 300˚C for 12 h reaching values of 90 kg/mm^2 approximately. Heat treatment with Ar atmosphere decreases the amounts of metal oxides formed. The quenching and tempering treatments affect positively the alloys hardness. The addition of metal oxide particles increases the electrical conductivity specifically in samples with 0.50 g of CuO_2 additions reaching average values on the order of 4.3×10^7 S/m. Obtained results indicate the possibility to use the alloys for fabrication of electrical conduction wires.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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